



Leaching of spent lead acid battery paste components by sodium citrate and acetic acid

Xinfeng Zhu^{a,b}, Xiong He^a, Jiakuan Yang^{a,*}, Linxia Gao^a, Jianwen Liu^a, Danni Yang^a, Xiaojuan Sun^a, Wei Zhang^a, Qin Wang^a, R Vasant Kumar^c

^a School of Environmental Science and Engineering, Huazhong University of Science and Technology (HUST), 1037 Luoyu Road, Wuhan, Hubei, 430074, PR China

^b Henan University of Urban Construction, Pingdingshan, Henan, 467000, PR China

^c Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, CB2 3QZ, UK

H I G H L I G H T S

- An alternative process that does not involve smelting or electro-winning was developed.
- PbO, PbO₂, and PbSO₄ can be prepared as Pb₃(C₆H₅O₇)₂·3H₂O with the optimal condition.
- Fast reaction rate and less consumption of sodium citrate are the virtues of this technology.

A R T I C L E I N F O

Article history:

Received 17 November 2012

Received in revised form 26 January 2013

Accepted 12 February 2013

Available online 19 February 2013

Keywords:

Spent lead paste

Leaching

Lead citrate

Recycling

Hydrometallurgical process

A B S T R A C T

A sustainable method, with minimal pollution and low energy cost in comparison with the conventional smelting methods, is proposed for treating components of spent lead-acid battery pastes in aqueous organic acid(s). In this study, PbO, PbO₂, and PbSO₄, the three major components in a spent lead paste, were individually reacted with a mixture of aqueous sodium citrate and acetic acid solution. Pure lead citrate precursor of Pb₃(C₆H₅O₇)₂·3H₂O is the only product crystallized in each leaching experiment. Conditions were optimized for individual lead compounds which were then used as the basis for leaching real industrial spent paste. In this work, efficient leaching process is achieved and raw material cost is reduced by using aqueous sodium citrate and acetic acid, instead of aqueous sodium citrate and citric acid as reported in a pioneering hydrometallurgical method earlier. Acetic acid is not only cheaper than citric acid but is also more effective in aiding dissolution of the lead compounds thus speeding up the leaching process in comparison with citric acid. Lead citrate is readily crystallized from the aqueous solution due to its low solubility and can be combusted to directly produce lead oxide as a precursor for making new battery pastes.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

In the past 15 years, the center of the international lead market has shifted to China which has emerged as the largest producer and consumer of primary and secondary refined lead. In 2010, the global consumption of secondary lead was 4.2 million tons, 80% of which was used for making lead-acid batteries in China [1]. Such large tonnage production is also associated with massive pollution arising from collection, sorting, treatment and refining of spent and discarded batteries. It is estimated that the amount of spent and discarded lead-acid batteries would be multiplied annually based on the mean lifetime of 2–3 years and will continue to grow especially in China and other emerging economies. A growing proportion of

the batteries are used in e-scooters with even lower average life-time. It is also reported that, in the case of China, more than 95% of spent and discarded lead-acid batteries are collected and recycled to reclaim the lead by pyrometallurgical methods for further lead batteries production.

Spent lead-acid batteries comprise four main parts: lead alloy grids, lead containing pastes, polymeric containers, and waste acids. Among them, spent lead paste, which is composed of lead sulfate, lead dioxide, lead oxide and a small % of metallic lead, create many difficulties in the subsequent recovery process [2,3]. Commonly, spent lead paste is recovered as metallic lead through an energy-intensive decomposition process, using traditional pyrometallurgical processes. Decomposition of PbSO₄ requires the action of high-temperature carbothermic reduction (>1000 °C), using coal, coke or natural gas as the source of reductant and energy, and therefore causing emissions of both SO₂ gas (from both the PbSO₄ and sulfur in the fossil fuel) and lead particulates

* Corresponding author. Tel.: +86 27 87792207; fax: +86 27 87792101.

E-mail addresses: jkyang@mail.hust.edu.cn, yjiakuan@hotmail.com (J. Yang).

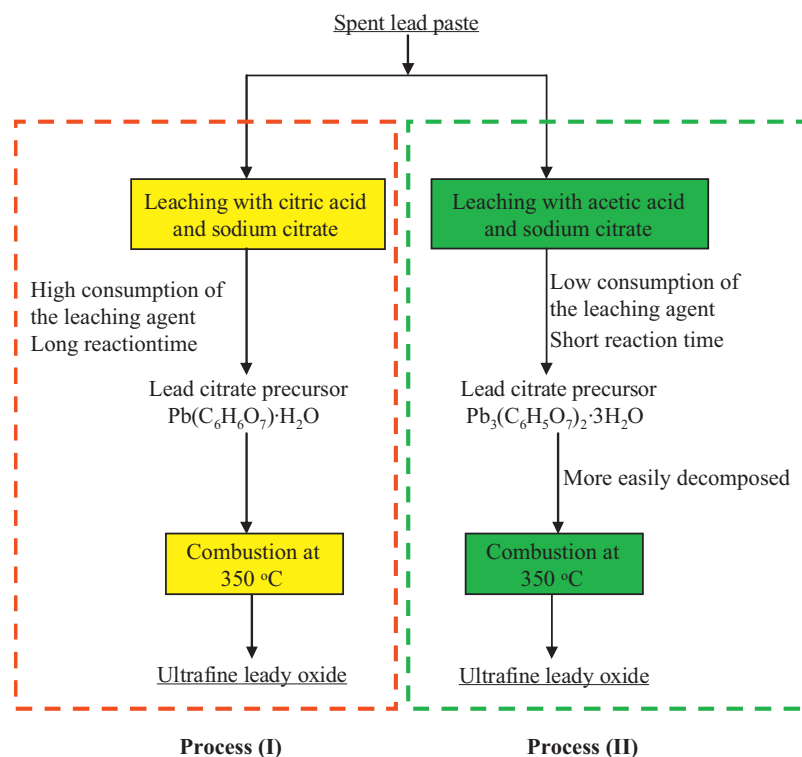


Fig. 1. Different procedures of leaching lead paste. Process (I): leaching process with the citric acid solution; Process (II): the new leaching process with acetic acid solution.

(from lead fuming at $T > 500^\circ\text{C}$) [4–11]. Metallic lead product is then re-oxidized to leady oxide for making lead pastes for new batteries.

More and more attention has been paid to hydrometallurgical approaches for recovery of lead from spent lead paste in spent lead-acid batteries. Conventional hydrometallurgical process flow comprises the following four steps. (1) Pretreatment process is used to separate spent lead paste from the plastic and metallic grid. (2) Spent lead paste is desulphurized by using Na_2CO_3 (aq), NaOH (aq) or $(\text{NH}_4)_2\text{CO}_3$ (aq) solutions [9,12,13], and the second most constituent of the paste PbO_2 , has to be reduced to Pb (II) to aid subsequent leaching by using H_2O_2 (aq), FeSO_4 or $\text{Na}_2\text{S}_2\text{O}_3$. (3) The desulphurized paste is then dissolved in powerful leaching agents such as fluoroboric acid (HBF_4) or H_2SiF_6 (aq) [9,14]. (4) Finally metallic lead is produced by electro-winning from the aqueous solution containing lead ions. Although SO_2 gaseous emission problem is solved, hazardous gases containing fluorine in the electro-winning process appear. Meanwhile, electro-winning process is capital intensive and often only suitable for large scale operations, which in turn entail large scale geographical movement of the hazardous battery waste materials. The net energy efficiency of electrochemical process is very low when account is taken of electricity generation at 30–40% efficiency from fossil fuel based power plants. For making new pastes, the metallic lead requires a re-oxidation step to form leady oxide.

Recycling of spent lead paste is an important subject, not only for the environmental protection, but also for the recovery of valuable materials. It is important to develop a process with potentially reduced environmental impact. A novel patented technology of recovering lead has been developed [15–17]. In this process, spent lead paste is treated with an aqueous citric acid and sodium citrate (or NaOH to help generate sodium citrate in situ) solution to generate a lead citrate precursor, which is then separated from the soluble sulfate solution. In this method, lead is then recovered after

calcining the lead citrate precursor in the form of ultra-fine lead oxide powder (containing a few % of metallic lead as demanded by specifications) that can be directly used for making new batteries thus circumventing the oxidation step from metallic lead [18]. This novel process is schematically shown in Fig. 1, and it is denoted as Process (I). Although this new process provides an alternative for the recovery of spent lead paste over traditional pyrometallurgical process, two major challenges still remain. Firstly, the current price of citric acid is around US \$850 per ton (subject to significant market fluctuations), which is much higher than other acids, such as sulfuric acid, hydrochloric acid, and acetic acid. Secondly, leaching rate with citric acid is relatively slow, which usually takes more than 8 h to finish the conversion of lead sulfate into lead citrate (due to low solubility of the lead citrate and the related low rates of both the dissolution of lead compounds and their subsequent crystallization). Therefore, despite all environmental benefits of using citric acid, its high reagent costs in combination with slow leaching and crystallization rates, can act as a deterrent for industrial application. The aim of this study is to minimize the amount of citric acid required while increasing the speed of producing the lead citrate precursor.

In this paper, as shown in Process (II) in Fig. 1, acetic acid in conjunction with sodium citrate was used in the hydrometallurgical process for recovery of spent lead paste. Acetic acid is the simplest carboxylic acid and is a lower cost carboxylic acid in comparison with citric acid which has been suggested in previous studies [16,17]. In this process, spent lead paste was treated with an aqueous acetic acid and sodium citrate solution to generate a lead citrate precursor, which was then separated from the solution. Lead could be recovered as ultra-fine lead oxide powder after the calcination of lead citrate precursor as demonstrated in previous work [16]. In this paper three major components (PbSO_4 , PbO_2 and PbO) individually initially and then jointly (using real industrial spent lead paste) were leached in a solution containing a mixture of acetic acid and sodium citrate. Optimal reaction conditions for

Table 1
Leaching conditions of PbO in the acetic acid–sodium citrate system.

No.	Molar ratio of sodium citrate to lead (α)	Molar ratio of acetic acid to lead (β)	Mass ratio of solid to liquid (S/L)	Leaching time (min)
A-PbO-I-1	2/3	2	1/7	10
A-PbO-I-2	4/3			
A-PbO-I-3	2			
A-PbO-I-4	2/3	2.4	1/7	
A-PbO-I-5	4/3			
A-PbO-I-6	2			
A-PbO-II-1	2/3	2	1/7	10
A-PbO-II-2		2.2		
A-PbO-II-3		3		
A-PbO-II-4		4		
A-PbO-III-1	2/3	2.4	1/7	2.5
A-PbO-III-2				5
A-PbO-III-3				15
A-PbO-III-4				30
A-PbO-III-5				60
A-PbO-IV-1	2/3	2.4	1/10	10
A-PbO-IV-1			1/20	

leaching/crystallization of lead compounds were researched in order to develop a cost effective and a high-yielding rapid leaching process for recycling spent lead paste.

2. Experimental

2.1. Chemicals

Analytically pure and commercially available chemicals were used to represent the components in spent lead paste in order to initially study the behavior of each component. Leaching experiments were carried out by using lead oxide (PbO), lead dioxide (PbO₂) and lead sulfate (PbSO₄) as individual starting materials. Industrial spent lead paste samples were provided by Hubei Jinyang Metallurgical Incorporated Co. Ltd, China, where the waste lead pastes were separated from spent lead-acid battery with MA31SS crushing and sorting machine made in USA. The paste was washed with distilled water to remove acid until the pH value of washed water was above 6.5. In this work, the particle size of the spent lead paste powders was <120 μm . Sodium citrate (Na₃C₆H₅O₇·2H₂O) and acetic acid (CH₃COOH) were used to prepare the leaching solution with distilled water for leaching/crystallization. During the leaching/crystallization experiments of PbO₂, hydrogen peroxide (H₂O₂, 30% purity) solution was used to reduce lead dioxide to PbO. All chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd, and used as received without further treatment.

2.2. Lead citrate synthesis from spent lead paste

Leaching experiments were carried out in a 250 mL glass beaker under constant magnetic stirring at 25 °C. First, leaching solutions of specified concentration were prepared, then, 10 g of solid lead compound or industrial spent lead paste was added to the mixed solution of acetic acid and sodium citrate, with a stirring speed of 500 rpm to maintain full suspension of the slurry. During the leaching, lead citrate began to crystallize from the solution. After completion of the reaction, any remaining solid (newly formed crystallites) was collected, washed with distilled water and dried at 65 °C to obtain the lead citrate precursor. In this process, sodium citrate contributed to the lead sulfate's desulfurization and crystallization, hydrogen peroxide facilitated reduction

of lead (IV) to lead (II) and acetic acid helped speed up the leaching process.

It is important to optimize leaching conditions primarily the dosage of leaching reagents, the starting mass ratio of solid lead compounds to liquid (referred to as S/L), and the leaching time in order to develop the new process for industrial trials. It should be noted that achieving maximum recovery of lead in the form of lead citrate crystal while minimizing the lead content in the residual solution is an important goal so that the residual solution can be recycled back in the flow-sheet with minimal treatment.

The leaching conditions pertaining to PbO and PbO₂ are listed in Table 1 and Table 2. Leaching and crystallization behavior of PbO in CH₃COOH and Na₃C₆H₅O₇·2H₂O solution was optimized by considering initial mole ratio of Na₃C₆H₅O₇·2H₂O to Pb (called as α), initial mole ratio of CH₃COOH to Pb (called as β), leaching time and solid/liquid ratio, S/L. The parameters, Na₃C₆H₅O₇·2H₂O/Pb mole ratio (α), initial CH₃COOH/Pb mol ratio (β), relative amounts of initial H₂O₂/PbO₂ mole ratio (γ), duration time and S/L ratio were investigated to optimize the leaching process for PbO₂. Leaching/crystallization efficiencies of PbO and PbO₂ were calculated from the lead content of the filtrate solution after removal of the lead citrate crystals.

In the process for leaching PbSO₄, the desulphurization efficiency is described in terms of two indices: the ratio of moles of sulfate ions in the filtrate solution to the original moles of sulfate in the reagent, and the proportion of lead remaining in the residual solution after treatment. Atomic Absorption Spectroscopy (WFX-100, Beifen-Ruili, China) was used to determine the percentage of lead remained in the filtrate, with respect to the original amount of lead in the starting lead compound. The analysis of the filtrate solution for SO₄²⁻ in the process of leaching PbSO₄ was performed through Ion Chromatography (DX-120, Dionex, USA). The desulphurization rate of PbSO₄ was calculated by the following Eq. (1).

$$\text{Desulphurization efficiency} = \left[\frac{(V_1 \times C_1)}{(W_1 \times 96/303)} \right] \times 100\% \quad (1)$$

where V_1 (L) is the volume of the filtrate, C_1 (mg/L) is the SO₄²⁻ concentration in the filtrate, W_1 (mg) is the mass of PbSO₄ sample, 96 is the molecular weight of SO₄²⁻, and 303 is the molecular weight of PbSO₄.

Table 2
Leaching conditions of PbO₂ in the acetic acid–sodium citrate system.

No.	Molar ratio of sodium citrate to lead (α)	Molar ratio of acetic acid to lead (β)	Molar ratio of hydrogen peroxide to lead (γ)	Mass ratio of solid to liquid (S/L)	Leaching time (min)
A-PbO ₂ -I-1	2/3	2	2	1/7	20
A-PbO ₂ -I-2	4/3				
A-PbO ₂ -I-3	2				
A-PbO ₂ -I-4	2/3	2.4	2	1/7	
A-PbO ₂ -I-5	4/3				
A-PbO ₂ -I-6	2				
A-PbO ₂ -II-1	2/3	2	2	1/7	20
A-PbO ₂ -II-2		2.2			
A-PbO ₂ -II-3		3			
A-PbO ₂ -II-4		4			
A-PbO ₂ -III-1	2/3	2.4	1	1/7	20
A-PbO ₂ -III-2			1.2		20
A-PbO ₂ -III-3			1.5		20
A-PbO ₂ -III-4			2.0		20
A-PbO ₂ -IV-1	2/3	2.4	1.5	1/7	2.5
A-PbO ₂ -IV-2					5
A-PbO ₂ -IV-3					10
A-PbO ₂ -IV-4					15
A-PbO ₂ -IV-5					30
A-PbO ₂ -IV-6					60
A-PbO ₂ -V-1	2/3	2.4	1.5	1/10	20
A-PbO ₂ -V-1				1/20	

The leaching conditions related to PbSO₄ are listed in Table 3. The parameters, initial mole ratio of Na₃C₆H₅O₇·2H₂O to Pb (called as α), initial mole ratio of CH₃COOH to Pb (called as β), leaching time and S/L were investigated to optimize the leaching process.

2.3. Characterization of lead citrate precursors

XRD patterns of the leached lead precursors were obtained by using X'Pert PRO X-Ray diffractometer (Philips, PAN alytical B.V., Holland) with Cu K α radiation with $\lambda = 1.5418 \text{ \AA}$ at a scanning rate of 0.28° per second for 2θ within the range from 5° to 75° . Thermal analysis of lead citrate precursor was carried out in alumina crucibles from room temperature to 600°C at the heating rate of $10^\circ\text{C min}^{-1}$ with an air flow of $20 \text{ cm}^3 \text{ min}^{-1}$ using Pyris1TGA (PerkinElmer, Perkin–Elmer Corporation, USA).

Table 3
Leaching conditions of PbSO₄ in the *n* acetic acid–sodium citrate system.

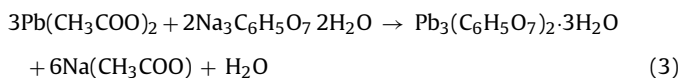
No.	Molar ratio of acetic acid to lead (β)	Molar ratio of sodium citrate to lead (α)	Mass ratio of solid to liquid (S/L)	Temperature ($^\circ\text{C}$)	Leaching time (min)
A-PbSO ₄ -I-1	1:2	2:1	1/5	25	120
A-PbSO ₄ -I-2	1:1				
A-S PbSO ₄ -I-3	2:1				
A-PbSO ₄ -I-4	3:1				
A-PbSO ₄ -I-5	4:1				
A-PbSO ₄ -II-1	3:1	2:3	1/5	25	120
A-PbSO ₄ -II-2		4:3			
A-PbSO ₄ -II-3		6:3			
A-PbSO ₄ -II-4		8:3			
A-PbSO ₄ -II-5		10:3			
A-PbSO ₄ -III-1	3:1	6:3	1/5	25	30
A-PbSO ₄ -III-2					60
A-PbSO ₄ -III-3					120
A-PbSO ₄ -III-4					180
A-PbSO ₄ -III-5					240
A-PbSO ₄ -IV-1	3:1	6:3	1/3	25	120
A-PbSO ₄ -IV-2			1/10		
A-PbSO ₄ -IV-3			1/20		
A-PbSO ₄ -V-1	3:1	6:3	1/5	35	120
A-PbSO ₄ -V-1				45	

3. Results

3.1. Leaching of PbO

Lead (II) oxide was leached with an aqueous solution of CH₃COOH and Na₃C₆H₅O₇·2H₂O. It was observed that lead citrate was rapidly formed and crystallized within the solution.

The reactions, as shown in Eqs. (2) and (3), were deduced from the previous leaching reaction between PbO and C₆H₈O₇·H₂O [16]. The leaching conditions of PbO listed in Table 1 were set on the basis of such reactions.



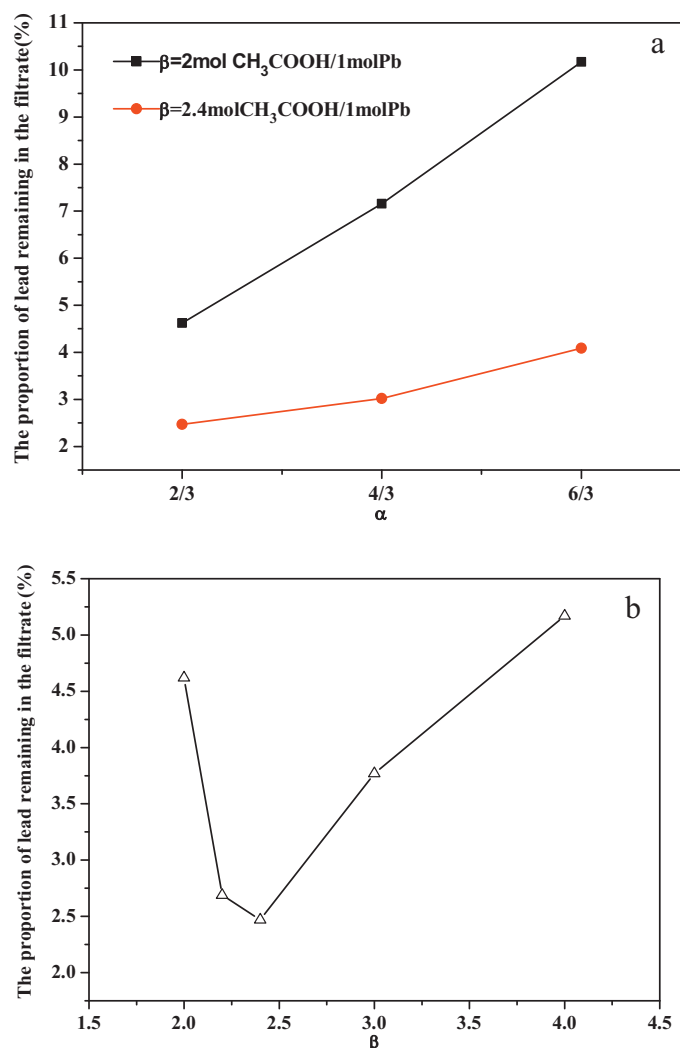


Fig. 2. The proportion of lead remaining in the filtrate for different initial α and β ratio (Leaching conditions (a): 10 min, 500 rpm, S/L = 1/7, 25 °C; Leaching conditions (b): $\alpha = 2/3$, 10 min, 500 rpm, S/L = 1/7, 25 °C).

The alkaline PbO is relatively difficult to be leached in aqueous $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ media. Thus the reagent CH_3COOH is needed to ameliorate this situation. It can be seen from Eq. (2) that, if β value is less than 2, insufficient amount of CH_3COOH will lead to incomplete neutralization reaction, thus allowing retention of non-reacted PbO in the filtered crystallites. Consistently, non-reacted PbO is observed in experiment even with leaching time beyond 60 min. Any contamination in $\text{Pb}_3(\text{C}_6\text{H}_5\text{O}_7)_2 \cdot 3\text{H}_2\text{O}$ can be readily deduced from XRD. Therefore, the values of β in the following experiments were set ≥ 2 . Similarly, the values of α were restricted no less than 2/3 in order to achieve the completed precipitation reaction as shown in Eq. (3).

When $\beta \geq 2$ and $\alpha \geq 2/3$, pure lead citrate $\text{Pb}_3(\text{C}_6\text{H}_5\text{O}_7)_2 \cdot 3\text{H}_2\text{O}$ can be obtained. As shown in Fig. 2(a), the lead content in filtrate increases as α value goes up from 2/3 to 6/3, which indicates the recovery ratio of lead decreases. It is reported that $\text{Pb}_3(\text{C}_6\text{H}_5\text{O}_7)_2$ can be partly dissolved in excess citrate ($\text{C}_6\text{H}_5\text{O}_7^{3-}$) solution [18]; therefore, the increase of lead content is resulted from high value of α which can result in unwanted dissolution of lead citrate. Fig. 2(b) shows that when β is equal to 2 and above, the proportion of lead remaining in the filtrate decreases firstly, but then increases together with the increment of β value, bottoming out at a β value of 2.4. This can be reasoned that sufficient CH_3COOH is essential to complete the neutralization reaction, while excessive

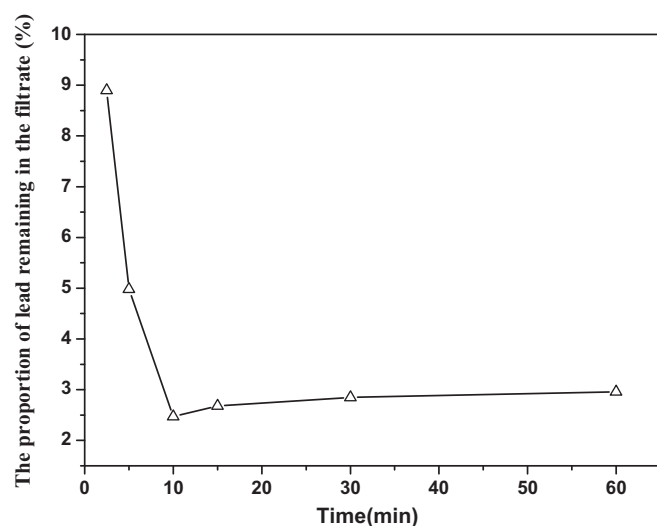


Fig. 3. The proportion of lead remaining in the filtrate with leaching time (Leaching conditions: $\alpha = 2/3$, $\beta = 2.4$, 500 rpm, S/L = 1/7, 25 °C).

amount affects adversely the lead citrate crystallization reaction as CH_3COOH can weaken the alkalinity of leaching solution. Thus, it is effective to reduce the lead content in filtrate by limiting α value of 2/3 and β value of 2.4. Other conditions are deduced as: time = 10 min, stirring speed = 500 rpm, S/L = 1/7 and temperature = 25 °C.

Fig. 3 presents the effect of reaction time on the variation of the proportion of lead remaining in the solution. As shown in the Fig. 3, complete precipitation is not achieved and the proportion of lead remaining in the filtrate is 8.92% after 2 min of leaching. However the proportion of lead remaining in the filtrate reaches the minimum value of 2.47% at a leaching time of 10 min. The dissolution of $\text{Pb}_3(\text{C}_6\text{H}_5\text{O}_7)_2$ in citrate ($\text{C}_6\text{H}_5\text{O}_7^{3-}$), is found to increase slightly when the leaching duration is increased beyond 10 min. The effect of S/L on the proportion of lead remaining in the solution shown in Fig. 4 is also studied under the condition of $\alpha = 0.67$ and $\beta = 2.4$. Insufficient water would result in the starvation of leaching media, while excessive water would cause increasing dissolution of lead citrate. A solid/liquid ratio (S/L) of 1/7 is found to be optimal for leaching and crystallization.

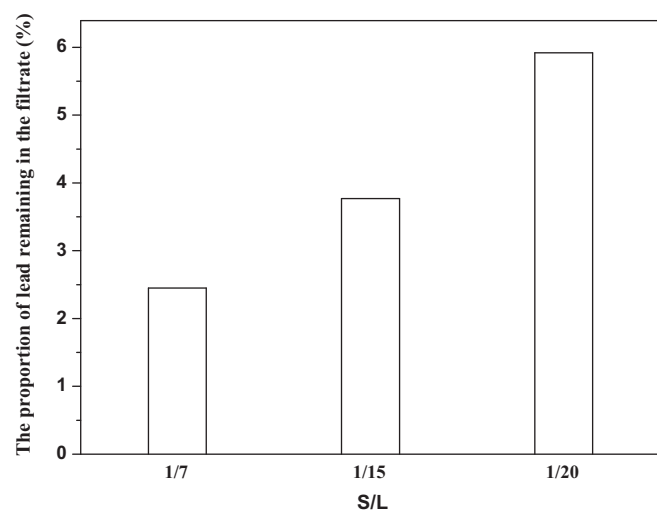
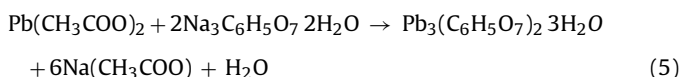
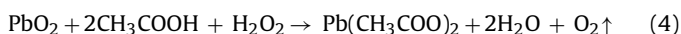


Fig. 4. Ratio of lead in the filtrate to total lead for different S/L (Leaching conditions: $\alpha = 2/3$, $\beta = 2.4$, 500 rpm, 10 min, 25 °C).

In summary, the optimal leaching conditions for PbO are α ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}/\text{Pb}$ mole ratio)=2/3, β ($\text{CH}_3\text{COOH}/\text{Pb}$ mole ratio)=2.4, S/L (solid/liquid ratio)=1/7 and leaching time = 10 min.

3.2. Leaching of PbO₂

It is difficult to dissolve PbO₂ in an aqueous media without being reduced from the Pb (IV) state to Pb (II) by using reducing agents such as H₂O₂ under the acidic leaching conditions. It was shown that PbO₂ can be effectively leached and then crystallized out as lead citrate ($\text{Pb}(\text{C}_6\text{H}_5\text{O}_7)_2 \cdot \text{H}_2\text{O}$) by a mixed solution consisting of $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ and H₂O₂ [16]. In this work, the leaching process of PbO₂ was studied in an aqueous solution of CH₃COOH and Na₃C₆H₅O₇ · 2H₂O and the corresponding reactions can be represented by the following reactions (4) and (5).



When only H₂O₂ or CH₃COOH solution is used to react with PbO₂, filtrate remains as unreacted PbO₂ after filtering with a small amount of lead in the solution. H₂O₂ is effective as a reducing agent for converting the insoluble Pb(IV) to the soluble Pb(II) oxide, thus accelerating leaching with CH₃COOH. It is found that with the assistance of H₂O₂, a minimum concentration of 0.67 mol of Na₃C₆H₅O₇ · 2H₂O and 2.4 mol CH₃COOH is required to convert a mole PbO₂ completely and produce uncontaminated Pb₃(C₆H₅O₇)₂ · 3H₂O product. As shown in Fig. 5(a), the proportion of lead remaining in the filtrate is found to increase with excess of sodium citrate [19]. Fig. 5(b) shows the proportion of lead remaining in the filtrate decreases firstly and then increases as β value increases.

Complete consumption of H₂O₂ is expected from stoichiometry for 1 mol of H₂O₂ per mol of PbO₂. Pure Pb₃(C₆H₅O₇)₂ · 3H₂O is obtained with the addition of 1.2 mol of H₂O₂ when reacted with 0.67 mol of Na₃C₆H₅O₇ · 2H₂O and 2.4 mol of CH₃COOH for each mol of PbO₂, under which condition the corresponding recovery was calculated to be 97.6%. When the initial H₂O₂ amount increases, the proportion of lead remaining in the filtrate does not change, as shown in Fig. 6.

Fig. 7 presents the effect of reaction time to the variation of the proportion of lead remaining in the filtrate. As shown in the Fig. 7, complete precipitation is not achieved, and the proportion of lead remaining in the filtrate is 5.75% after 5 min and 2.44% after 15 min. It is noted that excessive leaching duration would not increase recovery ratio of Pb₃(C₆H₅O₇)₂ · 3H₂O. By increasing the duration time, the proportion of lead remaining in the filtrate is further enhanced from 2.44% (15 min) to 2.61% (60 min). The proportion of lead remaining in the filtrate increases with the decreasing of starting S/L from 1/7 to 1/20, as shown in Fig. 8. Lower ratio (3.21%) of lead in the filtrate to total lead is achieved by leaching with a starting S/L of 1/7, responding to a maximum recovery of lead (96.8%) as pure lead citrate product.

In summary, the optimal leaching conditions of PbO₂ are: α ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}/\text{Pb}$ mole ratio)=2/3; β ($\text{CH}_3\text{COOH}/\text{Pb}$ mole ratio)=2.4; ratio of H₂O₂/Pb = 1.2; solid/liquid ratio (S/L) = 1/7; and a leaching time of 15 min.

3.3. Leaching of PbSO₄

Leaching of PbSO₄ with citric acid and sodium citrate solution followed by crystallization of lead citrate Pb₃(C₆H₅O₇)₂ · 3H₂O has been reported previously [17]. Results have shown that citric acid only played a role of buffer function in the leaching solution. In this

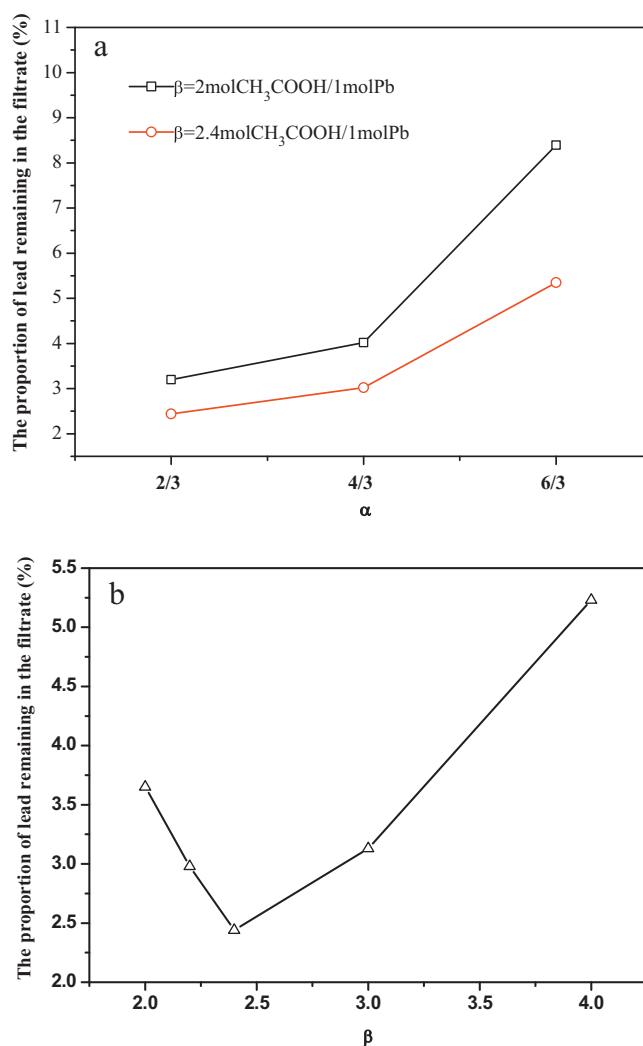


Fig. 5. The proportion of lead remaining in the filtrate for different initial α ratio of sodium citrate and β ratio of acetic acid (Leaching condition (a): $\gamma = 2$, 20 min, 500 rpm, S/L = 1/7, 25 °C; Leaching conditions (b): $\alpha = 2/3$, 20 min, 500 rpm, S/L = 1/7, 25 °C).

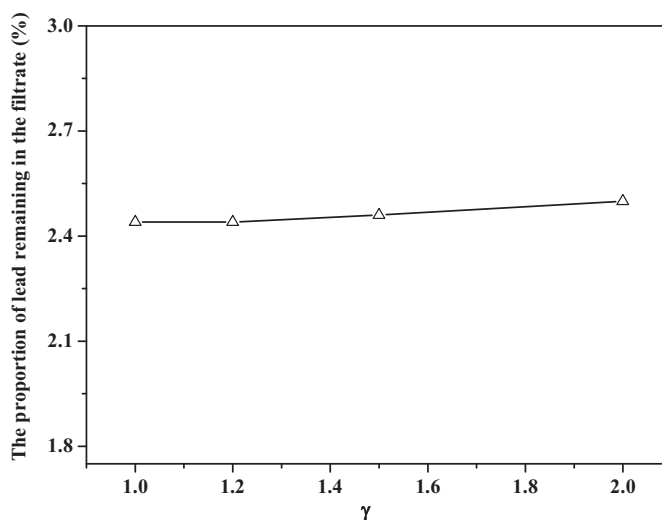


Fig. 6. The proportion of lead remaining in the filtrate for different initial H₂O₂ amounts (Leaching conditions: $\alpha = 2/3$, $\beta = 2.4$, 20 min, 500 rpm, S/L = 1/7, 25 °C).

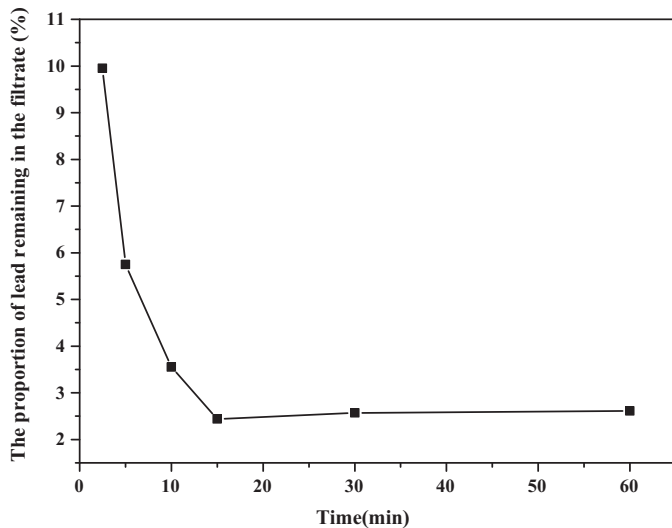
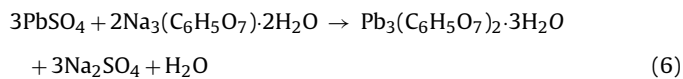


Fig. 7. The proportion of lead remaining in the filtrate of leaching PbO_2 with leaching time (Leaching conditions: $\alpha = 2/3$, $\beta = 2.4$, $\gamma = 1.5$, 500 rpm, $S/L = 1/7$, 25°C).

study, the critic acid was replaced by the cheaper acetic acid. The leaching process of PbSO_4 in an aqueous solution of CH_3COOH and $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ can be represented by the following reaction (6).



In a leaching solution containing 2 mol of $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ for each mol of PbSO_4 , the effect of CH_3COOH concentration on leaching is shown in Fig. 9. The proportion of lead remaining in the filtrate with respect to the initial lead from the sulphate, decreases to 4.3% (when 3 mol of CH_3COOH are added) from a value of 20% (when no CH_3COOH is added). Experimental study has shown that PbSO_4 can dissolve in the $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ solution in the leaching-crystallization process, and excess amount of $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ would result in a greater desulphurization efficiency of PbSO_4 and the higher proportion of lead remaining in the filtrate when S/L is $1/5$, temperature is 25°C and duration is 2 h. When α reaches a threshold value of $8/3$ the desulphurization efficiency is nearly 100% (Fig. 10). The proportion of lead remaining in the filtrate

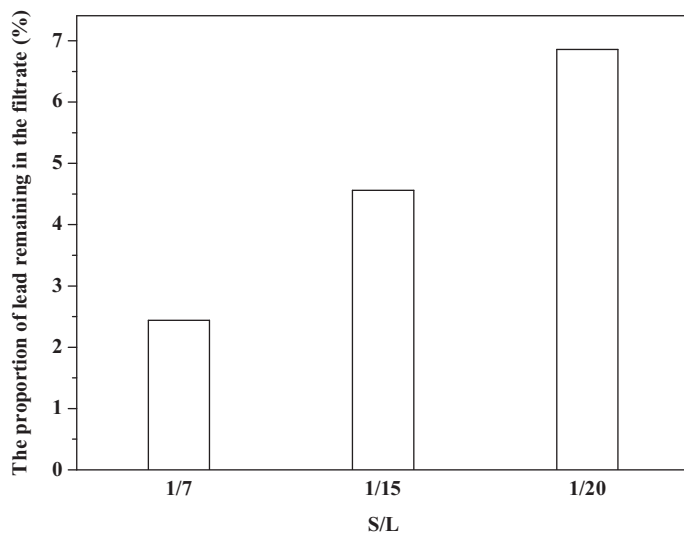


Fig. 8. The proportion of lead remaining in the filtrate of leaching PbO_2 with different S/L (Leaching conditions: $\alpha = 2/3$, $\beta = 2.4$, $\gamma = 1.5$, 500 rpm, 25°C).

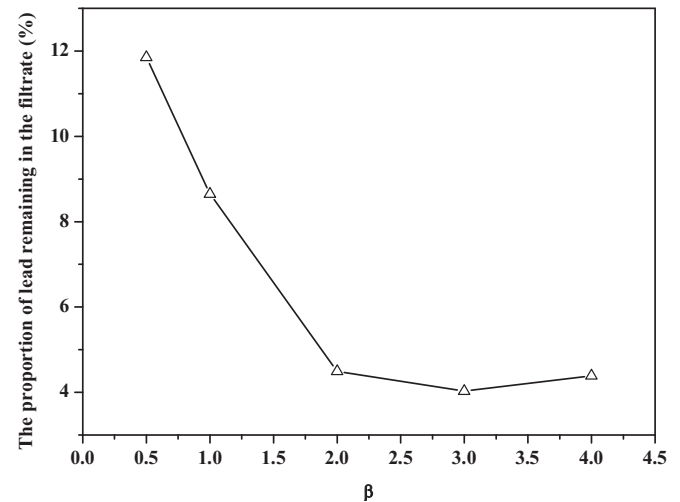


Fig. 9. The proportion of lead remaining in the filtrate of leaching PbSO_4 with different initial CH_3COOH amounts (Leaching conditions: $\alpha = 2$, 120 min, 25°C , $S/L = 1/5$, 500 rpm).

increases as α value goes up from $2/3$ to $10/3$. The figure suggests that α ratio of $6/3$ is enough for a 99.1% of desulphurization.

Fig. 11 presents the effect of reaction time on the variation of the desulphurization efficiency and the proportion of lead remaining in the filtrate. It is obvious that the longer the duration is, greater is the desulphurization efficiency. When the duration is 2 h, almost all the PbSO_4 has been converted. An increment of duration time from 30 min to 120 min results in the increase in desulphurization of PbSO_4 , from 83.8% to 99.7%. At the same time, the proportion of lead remaining in the filtrate varies only within a small range. Thus, it is reasonable to settle at 120 min as the optimal reaction time.

Full conversion of PbSO_4 is achieved when the S/L ratio is no less than $1/5$, such as $1/3$ in this study (Fig. 12). The proportion of lead remaining in the filtrate increases and the conversion ratio of PbSO_4 decreases with the decrease of the starting S/L ratio from $1/3$ to $1/20$, as shown in Fig. 12. Lower proportion (3.9%) of lead remaining in the filtrate is achieved by leaching with a starting S/L ratio of $1/5$ and $1/3$, with a maximum recovery of about 96% and a maximum desulphurization efficiency of 99.9%. Thus S/L ratio of $1/5$ proves to be the most appropriate for the leaching and crystallization process.

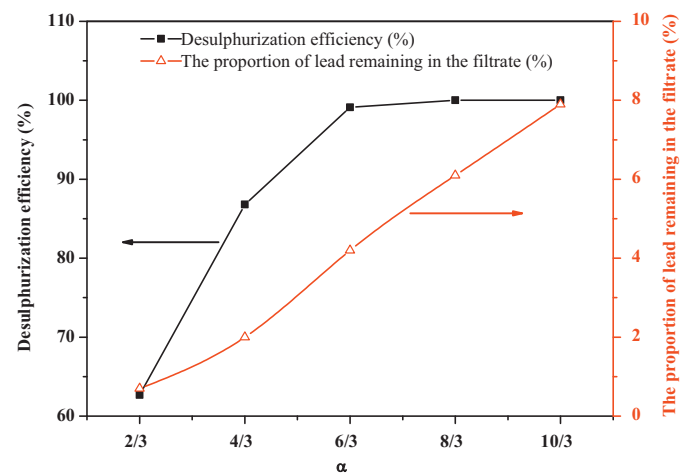


Fig. 10. Desulphurization efficiency of PbSO_4 and the proportion of lead remaining in the filtrate of leaching PbSO_4 with different α (Leaching conditions: $\beta = 3$, 2 h, 25°C , $S/L = 1/5$, 500 rpm).

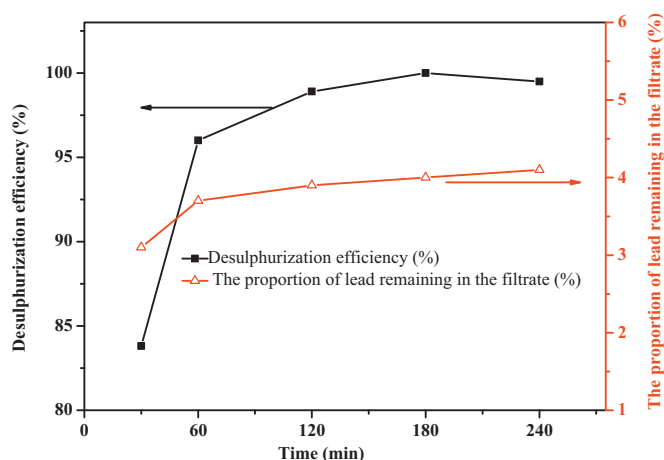


Fig. 11. Desulphurization efficiency of PbSO_4 and the proportion of lead remaining in the filtrate of leaching PbSO_4 with different leaching time (Leaching conditions: $\alpha = 2$, $\beta = 3$, 25°C , $\text{S/L} = 1/5$, 500 rpm).

3.4. Characterization of the precursors

X-ray diffraction patterns of lead citrate precursors obtained are shown in Fig. 13. The obtained patterns suggests that the products match with the precursor obtained from the leaching of PbSO_4 with $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ and $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ as reported previously [17]. These results suggest that under optimal conditions, lead citrate is more stable than sodium citrate, while sodium acetate is more stable than lead acetate, thus offering the desired selectivity for crystallizing lead citrate.

TG curves of lead citrate precursors obtained are shown in Fig. 14. The results of TGA prove that the precursors are more likely to be decomposed. The weight loss of the lead citrate precursors (from PbO , PbO_2 , PbSO_4) are 38.9%, 39.1% and 38.3% in the scanning range from 20 to 350°C . Stoichiometric calculations indicate that the composition of carboxylate from precursors can be expressed as $\text{Pb}_3(\text{C}_6\text{H}_5\text{O}_7)_2 \cdot 3\text{H}_2\text{O}$. Thus TGA data provide evidence for the leaching reactions as expressed in Eqs. (2)–(6).

3.5. Leaching of industrial spent lead paste

In order to demonstrate the applicability of the process to a real spent lead paste, 10 g of battery paste (chemical composition:

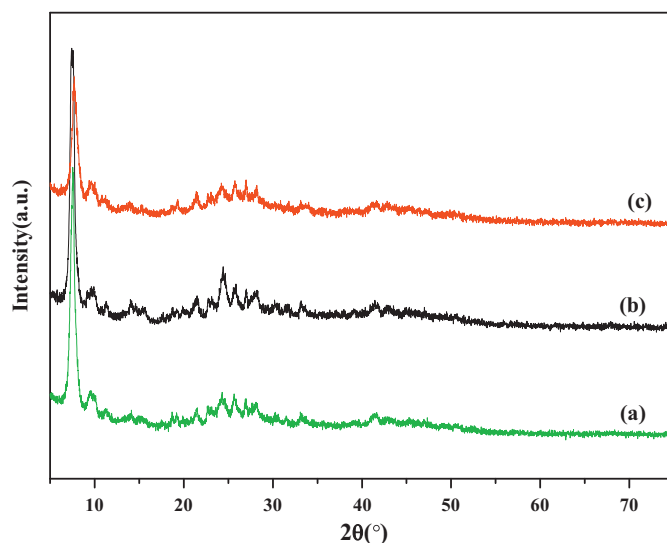


Fig. 13. Comparison of X-ray diffraction analysis of $\text{Pb}_3(\text{C}_6\text{H}_5\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$ from different lead compounds: (a) produced from PbO ; (b) produced from PbO_2 ; and (c) produced from PbSO_4 .

PbSO_4 : 64.5%, PbO_2 : 29.5%, PbO : 4.5%, Pb metal: 1.0%, rest: impurities) was leached with a solution containing 0.092 mol of CH_3COOH , 0.026 mol of H_2O_2 and 0.048 mol of $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$. The experiment was carried out for 120 min using 1/5 of S/L ratio at room temperature. After the experiment the mixture was filtered. The conversion ratio of spent lead paste reached a maximum value of 99.8%. Filtrate solution contained 2.23% of dissolved lead with a recovery of lead citrate of over 97.8%.

The reaction time and final products of PbO , PbO_2 , PbSO_4 and real spent lead paste as the starting material in different leaching solutions [16,17,19–21] are summarized in Table 4. As shown in Table 4, the reaction time of PbO , PbO_2 , and PbSO_4 with sodium citrate and acetic acid is found to be approximately 10 min, 15 min, 120 min and is shorter than the reaction time in sodium citrate and citric acid solution. Especially in the real spent lead paste of leaching process, shorter reaction time is of great practical and economic advantages.

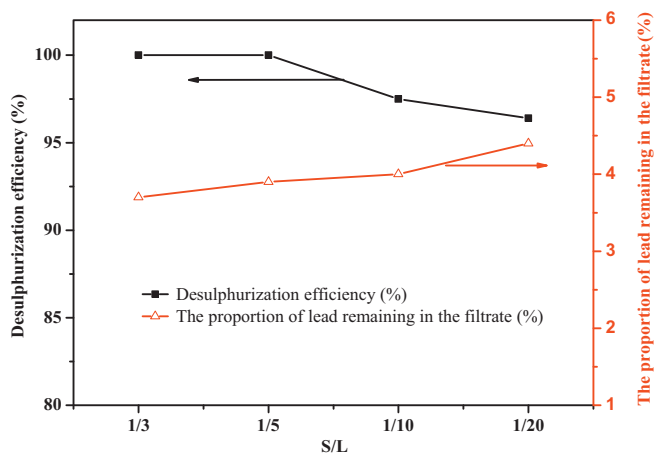


Fig. 12. Desulphurization efficiency of PbSO_4 and the proportion of lead remaining in the filtrate of leaching PbSO_4 with different S/L (Leaching conditions: 120 min, 2 h, $\alpha = 2$, $\beta = 3$, 25°C , 500 rpm).

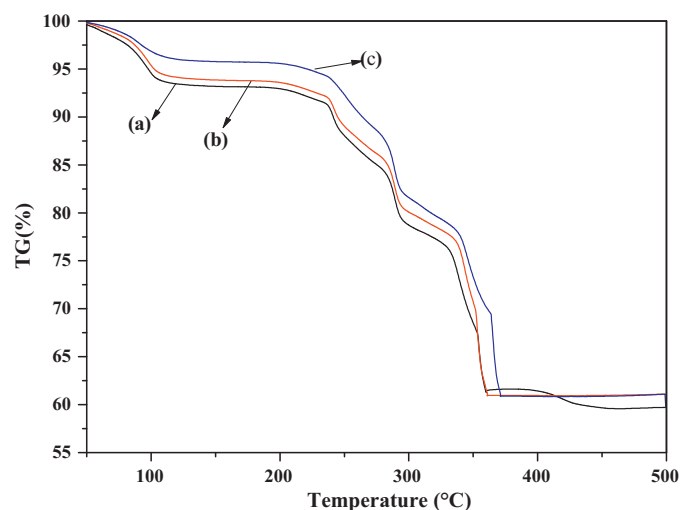


Fig. 14. Comparison of TG curves of $\text{Pb}_3(\text{C}_6\text{H}_5\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$ from different lead compounds in air: (a) produced from PbO ; (b) produced from PbO_2 ; and (c) produced from PbSO_4 .

Table 4

The reaction time and final products of the different starting materials.

Starting material		PbO	PbO ₂	PbSO ₄	Real lead paste
Sodium citrate and acetic acid solution	Reaction time	10 min	15 min	90 min	120 min
	Final product formula	Pb ₃ (C ₆ H ₅ O ₇) ₂ ·3H ₂ O	Pb ₃ (C ₆ H ₅ O ₇) ₂ ·3H ₂ O	Pb ₃ (C ₆ H ₅ O ₇) ₂ ·3H ₂ O	Pb ₃ (C ₆ H ₅ O ₇) ₂ ·3H ₂ O
Sodium citrate and citric acid solution	Reaction time	15 min	60 min	120 min	480 min
	Final product formula	Pb(C ₆ H ₆ O ₇)·H ₂ O	Pb(C ₆ H ₆ O ₇)·H ₂ O	Pb ₃ (C ₆ H ₅ O ₇) ₂ ·3H ₂ O	Pb(C ₆ H ₆ O ₇)·H ₂ O

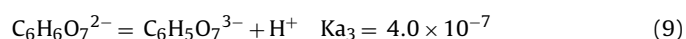
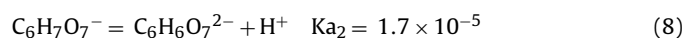
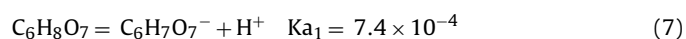
Table 5Dosages of leaching reagents for 10 g real lead paste (10⁻² mol).

Starting material	C ₆ H ₈ O ₇ ·H ₂ O	Na ₃ C ₆ H ₅ O ₇ ·2H ₂ O	CH ₃ COOH
Sodium citrate and citric acid solution	10.95	6.44	0
Sodium citrate and acetic acid solution	0	4.8	9.2

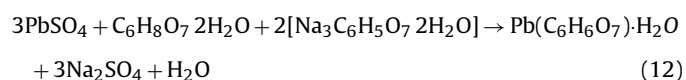
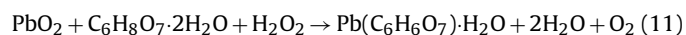
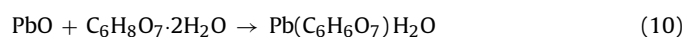
4. Discussion

The chemical formula of precursors in sodium citrate and citrate acid solution is Pb(C₆H₆O₇)·H₂O, and the chemical formula of precursor in sodium citrate and acetic acid solution is Pb₃(C₆H₅O₇)₂·3H₂O. C₆H₈O₇·H₂O and Na₃C₆H₅O₇·2H₂O are produced from biological sources and available at relatively high cost as industrial chemicals in food industry. In this work the lead citrate precursors are Pb₃(C₆H₅O₇)₂·3H₂O, and the requirement of C₆H₅Na₃O₇·2H₂O decreases by a factor of 3 thus greatly decreasing reagent costs. Results in this work can be used to underpin the development of a new economical and green process for recovering lead from lead battery pastes. From an economic point of view, Pb₃(C₆H₅O₇)₂·3H₂O can be selected in practical application. In addition, dosages of leaching reagents in sodium citrate and acetic acid solution are less than dosages of sodium citrate and citric acid solution (see Table 5 – values shown for 10 g spent lead-acid battery paste).

Citric acid is a common weak organic acid. One C₆H₈O₇ molecule contains three carboxyls and 3 mol H⁺ should be theoretically produced, upon dissociation of 1 mol citric acid in distilled water. But, H⁺ of the acid cannot be completely ionized. The dissociation reaction of citric acid can be expressed as following Eqs. (7)–(9), given along with values of the respective dissociation constants [22].



In different coexistence of citric acid and sodium citrate solution system, C₆H₈O₇, requiring illustration C₆H₇O₇⁻, C₆H₆O₇²⁻, C₆H₅O₇³⁻ ionic distribution is not the same [23–25]. Leaching of spent lead paste in citric acid can be described as three reactions. Under the synthesis condition, C₆H₇O₇⁻, C₆H₆O₇²⁻ and C₆H₅O₇³⁻ are the main ions in the solution. The leaching reaction of spent lead paste under the condition (1) may be given by the following reactions (10)–(12).



Three major components (PbSO₄, PbO₂ and PbO) in spent lead paste were individually leached in the solution of sodium citrate and acetic acid whose acidity was higher than that of citric acid [19]. The reaction can be represented by the Eqs. (2)–(6).

The acetic acid can accelerate the neutralization reaction speed of PbO₂, PbO during the leaching process and C₆H₅O₇³⁻ is a stronger complexing agent than C₆H₆O₇²⁻, which can speed up the complex-crystallization reaction, one of the fundamental processes in the leaching system of sodium citrate and acetic acid.

5. Conclusions

According to the experimental results, combined CH₃COOH/Na₃C₆H₅O₇·2H₂O reagents may be used as environmentally acceptable and financial affordable reagents. Leaching of PbO with 0.67 mol of Na₃C₆H₅O₇·2H₂O and of 2.2 mol of CH₃COOH solution per mol PbO for 10 min at 25 °C, with a starting S/L ratio 1/7 results in the crystallization of pure Pb₃(C₆H₅O₇)₂·3H₂O crystals. The lead content in the solution is 2.47% after crystallization, corresponding to a recovery of 97.53%. The leaching of PbO₂ with 0.67 mol of Na₃C₆H₅O₇·2H₂O, 2.4 mol of CH₃COOH and 1.5 mol of H₂O₂ for 15 min at 25 °C, with a starting S/L ratio of 1/7, also results in the precipitation of Pb₃(C₆H₅O₇)₂·3H₂O compound at an acceptable recovery of 97.43%. The optimum condition of the reactions are found to be 1 mol of PbSO₄ with a solution containing 2 mol of Na₃C₆H₅O₇·2H₂O and 3 mol of CH₃COOH for 60 min with a starting S/L ratio of 1/5. X-ray diffraction and thermal analysis of the precipitate after the leaching of the different lead compounds with a solution mixture of CH₃COOH and Na₃C₆H₅O₇·2H₂O show that it is Pb₃(C₆H₅O₇)₂·3H₂O. C₆H₈O₇·H₂O and Na₃C₆H₅O₇·2H₂O are produced from biological sources and available at relatively high cost as industrial chemicals in food industry. In this work the lead citrate precursors are Pb₃(C₆H₅O₇)₂·3H₂O, and thus the requirement of Na₃C₆H₅O₇·2H₂O is decreases by a factor of 3. Results in this work can be used to underpin the development of a new economical and green process for recovering lead from lead battery pastes.

Acknowledgements

The authors would like to thank the National Science Council of China (NSC 50804017), New Century Excellent Talents Project of Ministry of Education (NCET-09-0392), the Wuhan Planning Project of Science and Technology (20120321100), and the Key Program of Hubei Provincial Natural Science Foundation for Distinguished Young Scholars (2011CDA083) for the financial support. In addition, the authors appreciate the assistance from Analytical and Testing Center of Huazhong University of Science and Technology for providing the facilities to fulfill the experimental measurements.

References

- [1] X.F. Zhu, W.C. Liu, H.Y. Yang, L. Li, J.K. Yang, Preparation of ultrafine PbO powders from lead paste in spent lead acid battery, Chin. J. Nonferrous Met. 20 (2010) 132–136.
- [2] M.E. Stout, Secondary lead recovery from spent SLI batteries, in: J.B. Hiskey, G.W. Warren (Eds.), Hydrometallurgy Fundamentals, Technology and Innovation, Society for Mining, Metallurgy and Exploration, Littleton, U.S.A, 1993, pp. 1185–1195.
- [3] T.T. Chen, J.E. Dutrizac, The mineralogical characterization of lead acid battery paste, Hydrometallurgy 40 (1996) 223–245.
- [4] J.W. Elmer, The Basel Convention: effect on the Asian secondary lead industry, J. Power Sources 59 (1996) 1–7.

- [5] H. Valdez, Lead battery markets and recycling in Mexico and South America, *J. Power Sources* 67 (1997) 219–223.
- [6] S. Sobanska, N. Ricq, A. Laboudigue, R. Guillermo, C. Bremard, J. Laureyns, J.C. Merlin, J.P. Wignacourt, Microchemical investigations of dust emitted by a lead smelter, *Environ. Sci. Technol.* 33 (1999) 1334–1339.
- [7] M. Kreusch, M. Ponte, H. Ponte, N. Kaminari, C. Marino, V. Mymrin, Technological improvements in automotive battery recycling, *Resour. Conserv. Recycl.* 52 (2007) 368–380.
- [8] X.B. Ye, O. Wong, Lead exposure, lead poisoning, and lead regulatory standards in China, 1990–2005, *Regul. Toxicol. Pharm.* 46 (2006) 157–162.
- [9] N.K. Lyakov, D.A. Atanasova, V.S. Vassilev, G.A. Haralampiev, Desulphurization of damped battery paste by sodium carbonate and sodium hydroxide, *J. Power Sources* 171 (2007) 960–965.
- [10] A.M. Genaidy, R. Sequeira, T. Tolaymat, J. Kohler, M. Rinder, An exploratory study of lead recovery in lead-acid battery lifecycle in US market: an evidence-based approach, *Sci. Total Environ.* 407 (2008) 7–22.
- [11] K.M. He, S.Q. Wang, J.L. Zhang, Blood lead levels of children and its trend in China, *Sci. Total Environ.* 407 (2009) 3986–3993.
- [12] R.D. Prengaman, Recovering lead from batteries, *J. Metals* 47 (1995) 31–33.
- [13] R.D. Prengaman, C., Morgan, E., Hine, P., Homer, G.M. Griffin. US Patent, 2001 No: 6177056.
- [14] M. Olper, A full electrochemical approach in processing junk batteries, in: EDP Congress, Proceedings of TMS Annual Meeting, Denver, Colorado, USA, February 21st–25th, 1993, pp. 959–966.
- [15] R.V. Kumar, V.P., Kotzeva, S. Sonmez, Recovery of lead from lead waste such as lead battery paste, involves treating lead waste with aqueous citric acid solution, separating obtained lead citrate from solution and converting citrate into lead and/or lead oxide, in Cambridge Enterprise Ltd (Uyca) Univ Cambridge Tech Services Ltd (Uyca) WO2008056125-A1.
- [16] M.S. Sonmez, R.V. Kumar, Leaching of waste battery paste components. Part 1: Lead citrate synthesis from PbO and PbO₂, *Hydrometallurgy* 95 (2009) 53–60.
- [17] M.S. Sonmez, R.V. Kumar, Leaching of waste battery paste components. Part 2: Leaching and desulphurisation of PbSO₄ by citric acid and sodium citrate solution, *Hydrometallurgy* 95 (2009) 82–86.
- [18] L. Li, X.F. Zhu, D.N. Yang, L.X. Gao, J.W. Liu, R.V. Kumar, J.K. Yang, Preparation and characterization of nano-structured lead oxide from spent lead acid battery paste, *J. Hazard. Mater.* 203–204 (2012) 274–282.
- [19] B.J. Zhou, X.L. Wang, Reagent Chemicals, Guangdong Science & Technology Press, Guangzhou, 1988.
- [20] J.K. Yang, R.V. Kumar, D.P. Singh, Combustion synthesis of PbO from lead carboxylate precursors relevant to developing a new method for recovering components from spent lead–acid batteries, *J. Chem. Technol. Biotechnol.* 87 (2012) 1480–1488.
- [21] J.K. Yang, X.F. Zhu, R.V. Kumar, Ethylene glycol-mediated synthesis of PbO nanocrystal from PbSO₄: a major component of lead paste in spent lead acid battery, *Mater. Chem. Phys.* 131 (2011) 336–342.
- [22] S.S. Kety, The lead citrate complex and its role in the physiology and therapy of lead poisoning, *J. Biol. Chem.* 28 (1941) 181–192.
- [23] E. Bottari, M. Vicedomini, On the complex formation between lead (II) and citrate ions in acid solution, *J. Inorg. Nucl. Chem.* 35 (1973) 1269–1278.
- [24] E. Bottari, M. Vicedomini, On the complex formation between lead (II) and citrate ions in alkaline solution, *J. Inorg. Nucl. Chem.* 35 (1973) 2447–2453.
- [25] L.G. Ekström, Å. Olin, On the complex formation between lead (II) and citrate in acid, neutral and weakly alkaline solution, *Chem. Scr.* 79 (1978) 10–15.